



Test of a hydrodesulfurization catalyst in a biomass tar removal process with catalytic steam reforming



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ARTICLE INFO

Article history:

Received 16 December 2013

Received in revised form 24 February 2014

Accepted 4 March 2014

Available online 13 March 2014

Keywords:

Allothermal gasification

Tar reforming

Desulfurization

Hydrodesulfurization

Catalyst deactivation

ABSTRACT

In order to remove tars from a synthesis-gas produced with an allothermal, pressurized fluidized-bed biomass gasifier, a catalytic gas-cleaning-process is used. The tars are removed by means of catalytic steam reforming on a commercial nickel catalyst at temperatures of around 500 °C in a packed bed reactor. The synthesis-gas enters the reforming reactor at 300 °C. Due to the strongly exothermic methanation-reaction the catalyst bed heats up to temperatures high enough to achieve sufficient catalyst activity for tar reforming. Ni-catalysts are sensitive for sulfur poisoning, therefore the main sulfur component in the hydrogen-rich synthesis-gas, hydrogen sulfide (H₂S), is adsorbed in a packed bed reactor, filled with ZnO, upstream the tar reformer. Beside H₂S there are further sulfur compounds in the gas stream which cannot be removed efficiently by means of ZnO. The aim of this work is to investigate whether it is possible to use a commercially available Co–Mo catalyst for hydrodesulfurization (HDS) upstream the ZnO-bed in order to convert organic sulfur compounds into H₂S. Hydrodesulfurization processes are state-of-the-art in large-scale petrochemistry. The process-conditions in this common use-case differ from these in the application discussed within this work. To examine the ability of HDS in the process discussed here, specific HDS-tests and overall system tests were carried out with a synthesis-gas from a laboratory gasifier. The used synthesis-gas was produced with an allothermal fluidized bed gasifier with wood pellets as fuel. The HDS-catalyst started to show activity for hydrogenation of thiophene at a temperature of 350 °C under atmospheric pressure. The use of hydrodesulfurization showed a positive influence on the catalyst deactivation of the subsequent Ni-catalyst.

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1. Introduction

Because of the expected tremendous impact of climate change, caused by the utilization of fossil fuels, and the fact that the availability of these fuels is limited, it is necessary to change the ways of global energy production [1]. Therefore the usage of renewable energy sources becomes necessary. Biomass and agricultural waste are one of the renewable energy sources that should not only be used for heat supply like in most cases nowadays, but also for generating electricity or second generation bio fuels. In this regard, the gasification of biomass seems to be promising, especially due to the high process-efficiency and the suitability for decentralized energy production [2]. For thermochemical gasification various technologies can be taken into account. The allothermal fluidized bed steam

gasification of biomass which this paper deals with produces a high caloric synthesis-gas that mainly contains H₂, CO, CO₂, CH₄ and H₂O. Beside these main components, the gas also includes unwanted byproducts like particles, tars (C₆+ hydrocarbons), sulfur compounds, ammonia and alkali metal condensates [3].

Before the usage of the synthesis-gas in a gas engine or the processing into other fuels, the gas has to be cleaned from the main impurities. Especially the removal of the biomass tar is crucial, because the condensation of tars causes severe fouling in unheated plant components downstream the gasifier. Along with other methods, like for instance FAME-scrubbing, tar removal can be carried out by means of catalytic steam reforming on a Ni-catalyst at temperatures of about 500 °C [4–6].

The simplified catalytic tar removal method described here is especially suitable for decentralized small scale plants. In this process, after leaving the gasifier, the synthesis-gas is cooled down to 300 °C for filtration. At this temperature beside the coke-particles, also already condensed alkali-metal and other ash-particles can be removed. Almost the total tar load is in gaseous state.

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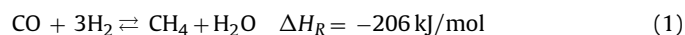


Fig. 1. Scheme of the discussed gas cleaning process.

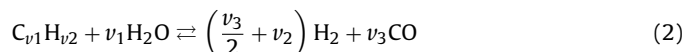
Fig. 1 shows the scheme of the here described gas cleaning process. The first reactor downstream the gasifier and the filtration of the synthesis-gas is the HDS Co–Mo catalyst. There hydrogenation and hydrodesulfurization reactions take place. Subsequent to this the H_2S -concentration in the synthesis-gas is reduced with ZnO in the second reactor. The aim of these first two steps is to reduce the total sulfur-load in the synthesis-gas, before entering the steam reforming nickel catalyst in the third reactor. In the following sections the single steps of the process are described in detail, beginning with the steam reforming of the biomass tars.

1.1. Catalytic steam reforming

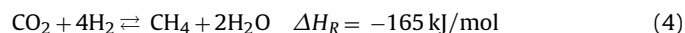
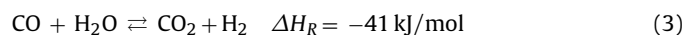
The gas enters the steam reforming reactor at 300°C , where the methanation reaction (1) and steam reforming of biomass tar take place on a nickel-based catalyst simultaneously. The occurring methanation-reaction (1) is strongly exothermic and heats up the gas to temperatures over 500°C [7].



This rise in temperature enables steam reforming of biomass tar, in order to generate hydrogen and carbon monoxide according to Eq. (2) [8].



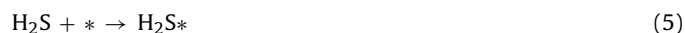
Beside the two mentioned reactions, also the water-gas shift reaction (3) and the Sabatier reaction (4) for reasons of balance, take place [8].



Catalytic reactions always lead to a certain deactivation of the catalyst used for the process. According to Bartholomew [9], there are different types of catalyst deactivation in general. In the catalytic process discussed in this paper, two mechanisms appear: Beside the deactivation by means of sulfur poisoning the Ni-catalyst, fouling of the catalyst caused by carbon or coke occurs.

1.2. Removal of hydrogen sulfide with ZnO

In order to reduce sulfur poisoning of the Ni-catalyst, it is reasonable to reduce the sulfur load upstream the steam reforming Ni-catalyst. In the raw synthesis-gas produced with an allothermal steam gasifier, hydrogen sulfide (H_2S) is the main sulfur component [10]. Various metal oxides are appropriate for desulfurization of biomass-based synthesis-gas [10–12]. For reasons of stability against the reducing atmosphere, the reachable desulfurization-concentration in equilibrium and the adsorption capacity, zinc oxide (ZnO) seems to be suitable for this process [8]. The adsorption of H_2S on ZnO is a chemisorptive process and described by Eq. (5), where * is the active surface site of ZnO.



The reachable equilibrium sulfur-concentration downstream the desulfurization-reactor strongly depends on the temperature of

the adsorbent. At 300°C , which is the catalyst's inlet temperature, it is possible to reach H_2S -contents far below 1 ppm_v, downstream the zinc oxide bed.

1.3. Hydrogenation and hydrodesulfurization

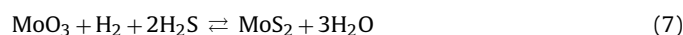
As mentioned above, H_2S is the main sulfur-component in the synthesis-gas. Besides H_2S , the gas also contains small amounts of other, mainly organic, sulfur components as carbonyl sulfide (COS), carbon disulfide (CS_2), thiophene ($\text{C}_4\text{H}_4\text{S}$) and benzothiophene ($\text{C}_8\text{H}_6\text{S}$). These cannot be removed effectively by ZnO. Sasaoka et al. [13] reported that COS can be partly converted to H_2S on ZnO at 500°C , but also the reverse reaction can occur. The organic sulfur species cause analog to H_2S deactivation of the Ni-catalyst in the downstream tar-reformer. To counteract this sulfur-related deactivation, a hydrogenation of the organic sulfur components seems to be possible. The HDS Co–Mo catalyst has to be integrated in the process upstream the H_2S -adsorption with ZnO. So the H_2S produced by the HDS Co–Mo catalyst can be removed with the ZnO-adsorbent.

Hydrodesulfurization is commercially used in large scale in oil refineries in order to convert organic sulfur compounds like mercaptanes or thiophenes to hydrocarbons and H_2S by means of hydrogen as reactant (Eq. (6)) [14,15].

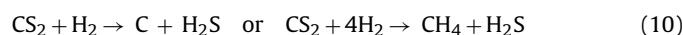


This process is carried out at temperatures between 300 and 425°C and medium to high pressures from 10 to 200 bar [14]. The used catalysts are based on molybdenum (Mo) with nickel (Ni) or cobalt (Co) as promoter (Co–Mo, Ni–Mo), mostly supported on Al_2O_3 , TiO_2 or $\text{SiO}_2\text{--Al}_2\text{O}_3$ [16–20].

The HDS-reaction needs two main catalyst functions. First, the hydrogenation of $\text{C}=\text{C}$ double bonds and following this the hydrogenolysis of C-S bonds, both reactions occur on the active MoS_2 sites. The HDS Co–Mo catalyst becomes active only in the sulfided state. Sulfidation of molybdenum oxide is described in Eq. (7) [16]. Whether the catalyst is pre-sulfided before use or not, has no influence on the maximum reachable activity, which is only determined by the sulfidation equilibrium [16,21]. Of course the hydrogen and H_2S in the feed gas can be used to sulfide the HDS Co–Mo catalyst.



The reactions to be catalyzed by HDS-catalysts are the hydrodesulfurization reactions of thiols like methanethiol or ethanethiol (8), thiophene (9), carbon disulfide (10), carbon oxy-sulfide (11) as well as the hydrogenation of olefins like ethene (12) [16].



Additionally to hydrogenation reactions, also the hydrolysis of CS_2 (13) and COS (14) occurs in the presence of steam [16].



There are several factors influencing the activity of HDS Co–Mo catalysts. The main factors are the temperature, the applied pressure, the gas hourly space velocity (GHSV) and the permanent gas-composition. A high hydrogen content in the synthesis-gas favors HDS, by contrast, a high steam content can lead to a slower sulfidation (Eq. (7)) of the catalyst because of competitive adsorption of H_2O and H_2S on the Mo surface [17].

Application of a HDS-catalyst for removal of organic sulfur in synthesis-gas from coal gasification for instance is described by Bhatia [16]. The used synthetic gas mixture contained CO , H_2 and N_2 with COS or thiophene ($\text{C}_4\text{H}_4\text{S}$) as exemplary sulfur compounds. Experiments with a gas mixture containing 130 ppm_v of COS were carried out at 370 °C, the conversion rate reached at a GHSV of 630 h^{−1} was 95%. The thiophene conversion rate of a synthetic gas containing 194 ppm of thiophene under atmospheric pressure was only 2% at 200 °C, but increased up to 92% at 450 °C. Under a pressure of 24 bar, a conversion rate of thiophene of over 97% could be reached within a temperature range between 275 and 475 °C [16].

Rabou and Bos [21] investigated the application of HDS Co–Mo catalysts for the hydrodesulfurization of biomass-based synthesis-gas using two commercial catalysts. They reported that it is possible to reduce the thiophene concentration in the synthesis-gas from 10 ppm_v to 0.1 ppm_v at atmospheric pressure. Additionally a hydrogenation of C_2H_2 , C_2H_4 , the conversion of thiols and activity for the water-gas shift reaction was observed. The catalysts inlet-temperature was set to 450 °C and increased to 550 °C in operation due to the exothermic water-gas shift and hydrogenation reactions. Generally the catalyst seemed to become active above 350 °C. They applied very low GHSV-values below 100 h^{−1}. According to Rabou et al. this leads to high catalyst-invest-costs, un-realistic for commercial application. The catalyst deactivation was not determined, but indications of a slow catalyst deactivation are reported [21].

The aim of this work is to investigate the activity of a commercial HDS Co–Mo catalyst implemented in the catalytic gas cleaning process described above. In contrast to Rabou and Bos [21] and Bhatia [16], the total sulfur concentration in the synthesis-gas used here with about 11 ppm is much lower. The hydrogen concentration in the synthesis-gas from the used gasifier is higher than in Rabou and Bhatia. This fact is positive for HDS, but the water content of over 40% is expected to have a negative influence.

Another major difference is the GHSV value applied. The results shown in this paper were obtained with much higher GHSV-values compared to the experiments explained in literature [21]. The values chosen here should be suitable for a commercial application. Too low GHSV lead to a disproportionate high amount of Co–Mo catalyst and consequently to uneconomic, high catalyst costs.

2. Experimental setup

HDS should be used as an extension to agnion's gas cleaning concept additionally to H_2S -desulfurization with ZnO and the catalytic steam-reforming of tars on a Ni-catalyst. The HDS-catalyst was tested with synthesis-gas from a laboratory scale biomass-gasifier under realistic process conditions. A commercially available, pre-sulfided Co–Mo catalyst in extruded form with a diameter of 1.5 mm was used in the test rig.

First specific HDS tests without desulfurization and tar-reforming were performed, in order to determine the influence of the temperature of the HDS catalyst. This way was chosen because the operation of such a catalyst was new and it was unknown if

the catalyst works at all at this conditions, so the aim was to keep the system as simple as possible. The second step was to perform overall system tests in order to investigate the impact of HDS integrated in the whole process chain – from gasification to catalytic tar reforming.

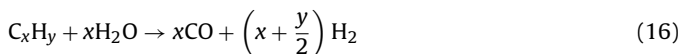
Fig. 2 shows the flow chart of the system used for the overall system tests. The gasifier and the experimental setup for the specific HDS-tests and the overall system tests are described in the following chapters.

2.1. Gasification setup

The gasifier used here is a small-scale pressurized, fluidized bed gasifier. As pictured in Fig. 2, the gasifier can be operated with air (autothermal) and/or with steam (allothermal) as fluidization- and gasification-agent. All tests discussed within this paper were carried out in the allothermal operation mode. The steam is generated in an electrically heated steam generator supplied with deionized water or recirculated condensate from the condenser downstream the tar reformer. The steam mass flow of 0.34 kg/h was measured by means of pressure measurement over an orifice and controlled by a pneumatic control-valve. This steam-flow corresponds to an excess-steam-ratio σ of 4 with the fuel power of 1.5 kW. The excess-steam-ratio σ is comparable with the air-excess-ratio λ in combustion and can be calculated as described in Eq. (15).

$$\sigma = \frac{X_{\text{H}_2\text{O}}}{X_{\text{H}_2\text{O},\text{min}}} \quad (15)$$

Thereby the minimum steam demand $X_{\text{H}_2\text{O},\text{min}}$ [kg_{H₂O}/kg_{Fuel}] is the mass of steam, which is necessary for the full reformation of 1 kg fuel to H_2 and CO according to Eq. (16).



A steam-excess-ratio σ of 1 means that enough steam for the reformation of the deployed biomass is present in the gasifier. Due to steam-reforming of the biomass tars with the Ni-catalyst, a steam-excess-ratio σ of 4 is necessary to prevent coking of the catalyst.

As feedstock, wood pellets according to [22] with a water content of 6% are used. The feed mass flow is 0.3 kg/h; this corresponds to a fuel power of 1.5 kW. Fuel is transported from the storage container to the reactor with a screw conveyor and a chute (cf. Fig. 2). The pellets storage is rinsed with nitrogen in order to prevent the diffusion of synthesis-gas into the chute and the pellets storage. Water and tar from the synthesis-gas would condense and cause clogging of the system. Due to this rinsing, the synthesis-gas contains about 22% N_2 .

The gasification takes place in a reactor externally heated at about 820 °C. For the heat supply an external tube-furnace is installed. Coke and ash particles are removed from the synthesis-gas by a sinter-metal candle filter downstream the reactor at 350 °C. The gasifier is operated 1 bar above atmospheric pressure, in order to overcome the pressure drops of the reactors and instruments downstream. The pressure is controlled by a regulation-valve downstream the filter.

2.2. Gas cleaning test setup

The gas cleaning test rig (see Fig. 2) consisted out of 3 reactors, heated by heating tapes up to the desired temperatures. All reactors and piping are made of stainless steel. The gas cleaning test-rig is not pressurized. As a result of the pressure losses in the reactors, the inlet pressure of the test rig is about 70 mbar.

Reactor 1 contains the HDS Co–Mo catalyst and is heated to 450 °C at the overall system tests. The temperature in the middle of

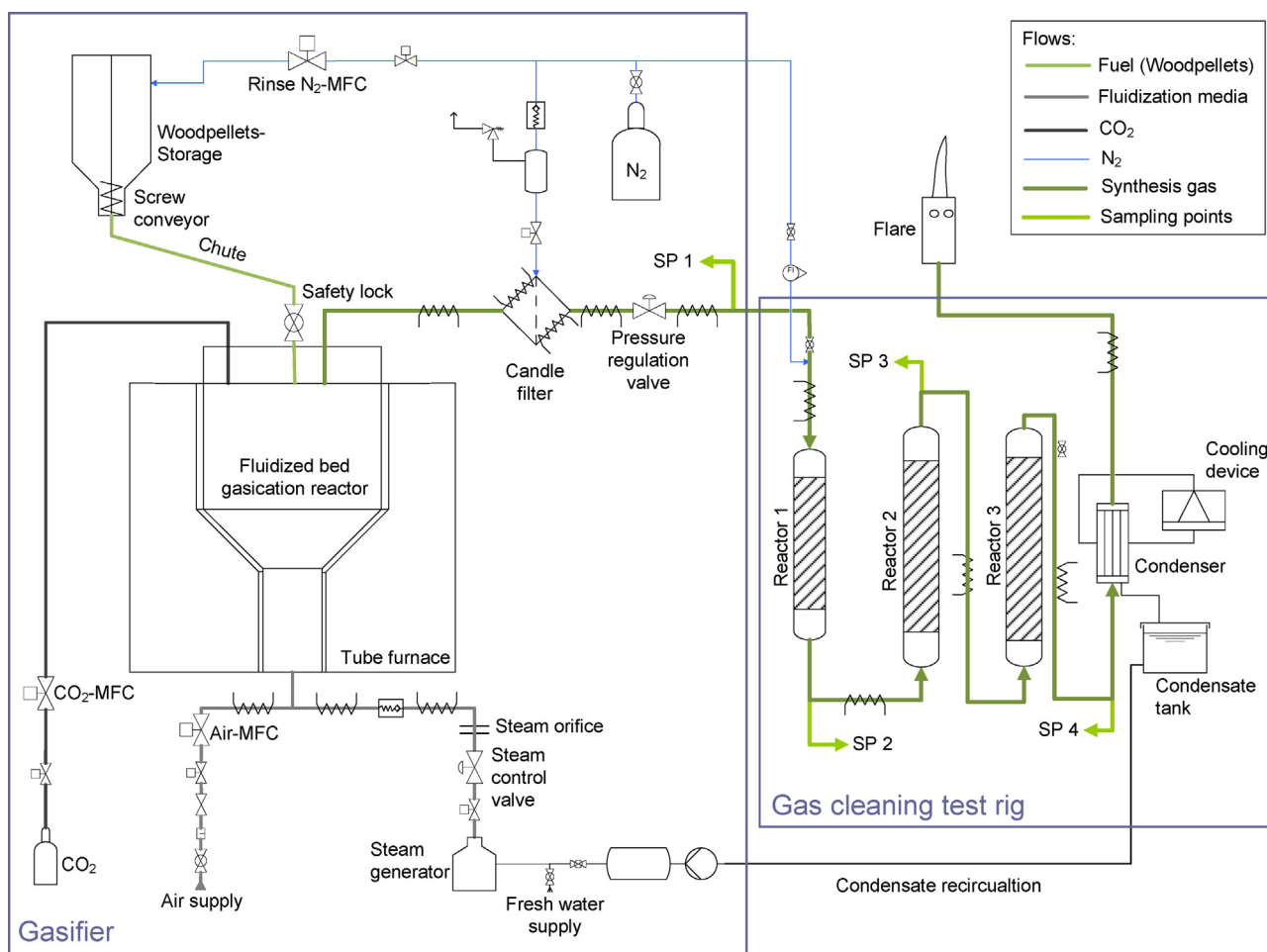


Fig. 2. Flow chart of gasifier and gas cleaning test rig.

the packed catalyst bed is measured with a thermocouple. The reactor was filled with 210 ml of a commercially available HDS Co–Mo catalyst in extruded form, supported on Al_2O_3 , containing between 2.5% and 10% cobalt and 20–25% molybdenum. These operation conditions lead to a GHSV of 4400 h^{-1} in the HDS-reactor.

In the isothermal reactor 2 (see Fig. 2), the H_2S in the synthesis-gas is adsorbed on ZnO at a temperature of 300°C . The reactor contains 1100 ml of commercially available ZnO-adsorbent in pelleted form. The H_2S concentration in equilibrium at this temperature is far below 1 ppm.

Catalytic steam reforming of the biomass tar in the synthesis-gas is done by means of a Ni-catalyst applied in reactor 3 (see Fig. 2). The synthesis-gas enters the catalytic bed at 300°C . Due to the occurring exothermic methanation reaction, the gas heats up to 510°C . During operation, the tar-reforming-reactor does not need to be heated. The temperature profile in reactor 3 is measured continuously by twelve thermocouples at intervals of 10 mm placed in a thermowell in the middle of the catalyst bed. The temperature profile in the reactor is a measure for the catalyst activity and therefore used for the determination of the catalyst deactivation. Synthesis-gas with low tar-content leaves the reactor at 500°C and is cooled in a condenser to about 30°C in the laboratory tests. The condensate can be recirculated within the process and therefore is fed into the steam generator of the gasifier.

In the specific HDS-tests, only the HDS catalyst was examined. For reasons of better temperature control and monitoring, the Co–Mo catalyst was loaded in reactor 3 of the gas cleaning test rig pictured in Fig. 2. In these tests the reactor was filled with 100 ml

inert ceramic particles at the inlet and the outlet respectively, with 150 ml HDS-catalyst packed in between. Reactors 1 and 2 were bypassed. The condenser (see Fig. 2) also was by-passed to prevent fouling due to the tar-condensation. The specific HDS-tests were done in a temperature range between 300°C and 510°C at a fixed GHSV of 6200 h^{-1} .

2.3. Analytics

There are four heated gas sampling points arranged (cf. Fig. 2) in the facility. At this points the gas for the measurement of the permanent gas composition, the tar load and sulfur components was sampled. Sampling of synthesis-gas was done alternately at all four sampling points. The sampled gas was sucked through a number of impinger bottles filled with water, FAME and isopropyl alcohol in order to condense water and remove tar. The synthesis-gas was analyzed by means of an ABB AO2020 [23] gas analyzer measuring CO , CO_2 , CH_4 , O_2 and H_2 . H_2S was measured by a colorimetric online detector (Sick Monocolor 1N) [24]. Tar sampling was carried out with the SPA-method [25], using Bakerbond SPE 7088-03 tubes as tar sorbent. With a syringe pump in a sampling time of about 30 min, about 100 ml of synthesis-gas was routed through the adsorbent. The SPE tubes were extracted with acetone and analyzed in a Varian CP 3800 GC-FID system [26], with a CP-Sil 5 CB column.

Organic sulfur compounds like thiophene or benzothiophene were also sampled via the same SPA-method. The used method is suitable for the measurement of volatile species like thiophene

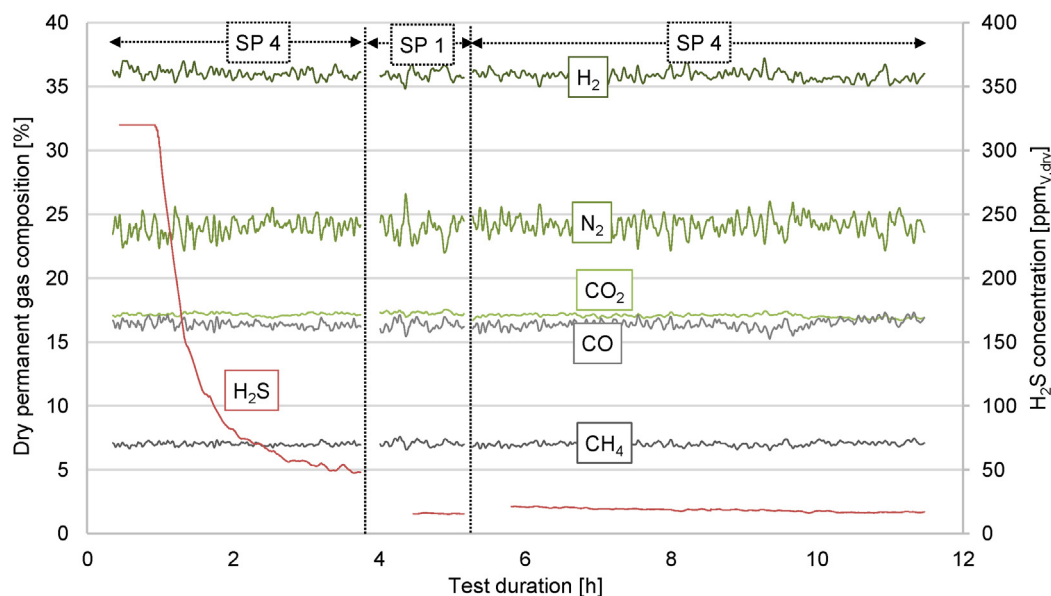


Fig. 3. Development of H₂S concentration after experiment started.

when the samples are stored in a freezer until extraction to prevent vaporization of the volatile components. The reliability of this method was checked by the comparative measurement of samples which were sampled at the same time but extracted and analyzed at different times. The analysis was carried out with another CP 3800 GC; the used detector here was a sulfur-selective pulsed flame photometric detector (PFPD). The deviation of the GC-analysis was below 3%.

The measurement of olefins was done with Dräger Short-term Tubes CH31201 at the outlet of the gas analyzer system; the accuracy of the Short-term Tubes is $\pm 10\%$ [27].

3. Results and discussion

3.1. Synthesis-gas composition of the gasifier

During all tests the gasifier was operated in the working point described in Section 2.1. The conditions above lead to a measured average dry synthesis-gas composition of 22.8% N₂, 17.2% CO₂, 16.5% CO, 7.0% CH₄ and 36.5% H₂. By means of mass balancing, the steam content and the synthesis-gas volume flow were calculated. The steam content in the gas after the gasifier was approximately 42%. The overall volume flow was 0.93 m³/h at standard conditions, volume flow and permanent gas composition fluctuated lightly because of discontinuities in fuel insertion. Fuel was fed once every minute into the fluidized bed. In the long run, the concentrations of the permanent gases stayed constant and varied about $\pm 0.5\%$. The concentration of H₂S, also measured in the dry gas flow, is about 17 ppm_V. The tar load of the produced gas varied between 6 and 10 g/Nm³, whereas C₆-components like benzene, toluene and xylene (BTX) are not considered as tar. The tar-like organic sulfur components thiophene and benzothiophene are detected in the liquid samples from SPA-method with the GC-PFPD. The sum concentration of these is below 0.9 ppm_V.

3.2. Specific HDS-tests – influence of the operation temperature on HDS activity

As mentioned above, the specific HDS-tests were done in order to study the influence of the operation temperature on

the activity of the HDS-catalyst. The Co–Mo catalyst was heated up to the desired operation temperature under nitrogen purge with a temperature gradient of 25 K/h. After a stationary gas-concentration was measured for several hours, the experiment was started. In the experiment the permanent gas composition and the H₂S-concentration up- and downstream the HDS-catalyst was measured. It was observed that the H₂S-content increased to higher levels compared to the concentration in the feed-gas for several hours due to sulfur desorption from the catalyst at elevated temperatures, this occurs because exothermic adsorptive processes are favored at lower temperatures.

Before some of the specific HDS-tests, the HDS-catalyst was additionally presulfided with a mixture of 250 ppm_V H₂S in N₂. After presulfidation and streaming with synthesis-gas, the increased H₂S-concentration was more pronounced, but after 10–20 h of operation the same H₂S levels as without presulfiding were observed. This is shown in Fig. 3 for a test at 300 °C HDS operation temperature. The H₂S concentration at sampling point 4, downstream the HDS-catalyst, increased after starting the experiment to more than 320 ppm, which was the upper range value of the used analyzer. After some hours the value decreased to 20 ppm. This value corresponds to the H₂S-adsorption equilibrium-concentration on the catalyst, determined by temperature, pressure and the composition of the gas phase. For comparison also a measurement at sampling point 1, downstream the gasifier was done. The gas composition at this point showed a H₂S-concentration typical for the gasifier, Fig. 3 also shows that in this case there was no change in permanent gas composition due to the HDS-catalyst.

The permanent gas composition measured at a test at a HDS-temperature of 510 °C is plotted in Fig. 4. The fluctuations in the measured values result mainly from the discontinuous fuel input. The gray shaded areas in Fig. 4 show the gas composition measured downstream the HDS-reactor at sampling point 4 (cf. Fig. 2), the unshaded sections at the outlet of the gasifier. The measured average H₂S-concentration at sampling point 1 downstream the gasifier was with 17 ppm constant over the whole duration. At the beginning the H₂S concentration downstream the HDS-reactor was significantly higher; this was due to the presulfidation-effect explained above. After test-hour 70 the H₂S-concentration

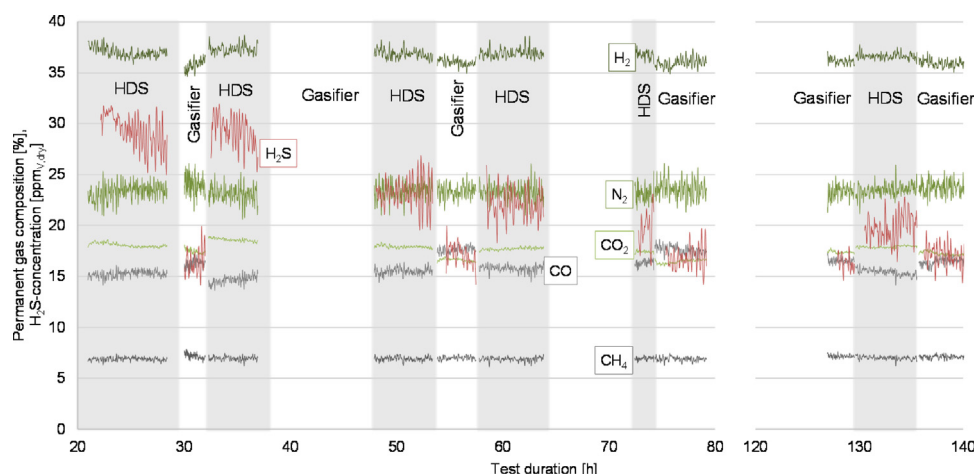


Fig. 4. Permanent gas composition of a HDS-test carried out at 510 °C.

downstream HDS was constant for the remaining test. This indicates that the increase of H_2S (compare shaded and unshaded areas) results from the conversion of organic sulfur components to H_2S .

It can also be seen that a slight difference in the concentrations of CO , CO_2 and H_2 occurred. Downstream the HDS-catalyst, CO_2 and H_2 -values were higher, the CO -concentration was lowered compared to the dry gasifier gas. This happened due to the exothermic water-gas shift reaction (Eq. (3)) occurring at this temperature on the HDS-catalyst.

As seen in Fig. 4, the H_2S -concentration increased with rising temperatures of the HDS-catalyst. The increase is a measure for the catalytic activity for HDS. The differences in the measured H_2S -values between the sampling points up- and downstream HDS are shown in Fig. 5 as a function of the packed-bed temperature in the reactor. At 300 °C the catalyst showed no catalytic activity. With rising temperature the catalytic activity increased. The variations of the H_2S -increase in Fig. 5 were partly caused by fluctuations of the gasifier's gas composition, it was not possible to measure the H_2S -concentrations simultaneously (cf. Fig. 4).

The test at 510 °C was carried out twice, first with a used HDS-catalyst and the second time with a new catalyst. With the new Co–Mo catalyst the H_2S -generation was much higher than with a catalyst that was used for several hundred hours. A possible reason therefore is catalyst deactivation effects, however the stability of the catalyst and possible degradation effects were not investigated within this work.

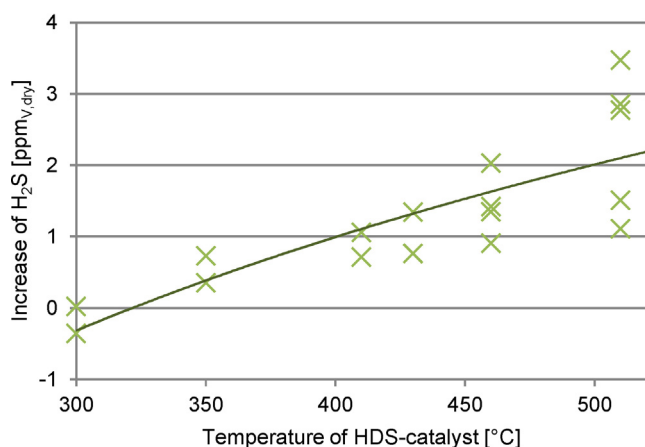


Fig. 5. Increase of H_2S in dependence of HDS operation temperature.

In Fig. 6 the measured values of the thiophene concentration in the synthesis-gas at different sampling points are pictured. As explained in the experimental setup section, the values were determined from SPA-samples and analyzed with a GC-PFPD. The concentration of thiophene in the synthesis-gas downstream the gasifier (SP 1) varied between 0.23 and 0.86 ppm. Also the results from analysis downstream the HDS-catalyst (SP 4) vary, besides the temperature-influence, the measured thiophene-concentration also depends on the concentration upstream the HDS-reactor. In order to obtain specific information of the temperature-influence, a thiophene conversion-rate as function of temperature was calculated, cf. Fig. 7. At 300 °C no conversion was observed, but with rising temperature, similarly to the increase of H_2S shown in Fig. 5, the conversion rose as a fact of increased catalytic activity. Between 430 °C and 510 °C, thiophene conversion rates between 35 and 67% were reached. These rates were not as high as the values reported by Rabou and Bos [21]. A possible reason therefore is the much lower residence-time at the HDS-catalyst in the experiments discussed here.

Within all tests shown here, the concentrations of the organic sulfur compounds 2-methylthiophene, 3-methylthiophene and dibenzothiophene were under the detectability (<0.1 ppm) of the GC-PFPD-system.

Also the measurement of olefins (unsaturated hydrocarbons) was carried out several times in all specific HDS-tests. The concentration of olefins measured at sampling point 1 varied between

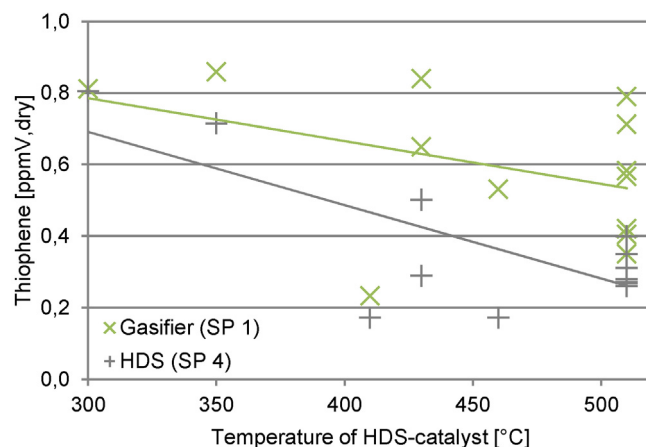


Fig. 6. Thiophene concentration before and after HDS-catalyst.

Table 1
Synthesis-gas compositions of overall test (HDS 2) with HDS at sampling points (SP) 1–4.

Volume fraction	SP 1: gasifier		SP 2: HDS		SP 3: desulfurization		SP 4: tar reformer	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
N ₂ (vol.%)	22.8	13.2	22.7	13.2	23.1	13.4	21.4	14.5
CO ₂ (vol.%)	17.2	10.0	17.4	10.2	17.6	10.2	29.3	19.9
CO (vol.%)	16.5	9.6	16.0	9.4	15.8	9.2	2.7	1.8
CH ₄ (vol.%)	7.0	4.1	6.9	4.1	7.0	4.1	18.5	12.5
H ₂ (vol.%)	36.5	21.3	37.0	21.7	36.5	21.2	28.1	19.0
H ₂ O (vol.%)		41.8		41.4		41.9		32.3
H ₂ S (ppm _v)	17.0	9.9	17.4	10.2	0.1	0.1	<0.1	<0.1

0.9 and 1.3% propene-equivalent value. Comparative measurements with a micro-GC showed that the values obtained with the Dräger short-term Tubes correspond to the sum of concentration of ethene and ethyne. Against the expectations almost no conversion of olefins like ethene (cf. Equation 6) was measured downstream the HDS-catalyst. The simultaneous measurements at SP 1 and SP 4 showed the same concentrations at the conditions discussed here. A hydrogenation of olefins was not measured, but ongoing work is focused on this issue. Perhaps the measurement method with the Dräger Short-term tubes was too inaccurate. A possible conversion of ethyne to ethene also cannot be measured by using this method.

The comparison of the measurements of H₂S and thiophene in the specific HDS-tests shows that the sulfur balance is not even if only these two values are considered. The increase of H₂S is higher than the decrease in thiophene. The reason for this is not clear in detail, but in the measurements shown here, a lack of information about other volatile sulfur compounds like COS and CS₂ occurs. Possibly these sulfur species, probably also present in the synthesis-gas, are converted into additional H₂S. However, a statement about the activity of the catalyst and its dependency of temperature can be made: The activity of the HDS-catalyst rises with rising temperature and below 350 °C no activity was observed.

3.3. Overall system tests

The overall system tests included the whole gas cleaning setup described in Section 2.2 (cf. Fig. 2). These tests should determine the effects of HDS on the catalyst deactivation of the subsequent Ni-catalyst. The specific HDS-tests showed that there is no activity of the HDS-catalyst below 350 °C, but the activity increased with higher temperatures. The HDS-catalyst was operated at 450 °C in the overall system test due to good conversation rates at this temperature.

Three long term tests were carried out in order to determine the influence of HDS on the catalyst deactivation. Prior to the start

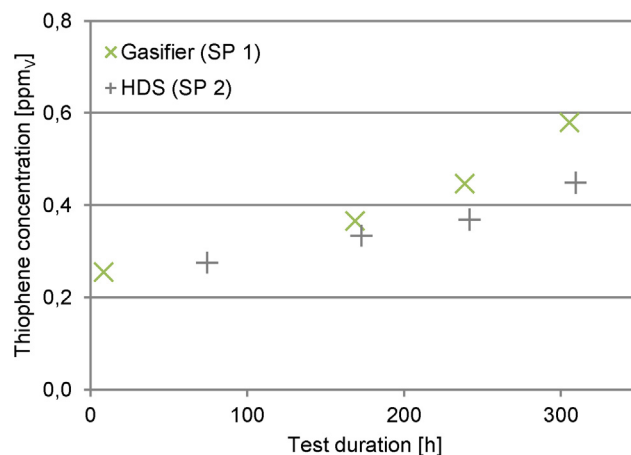


Fig. 8. Thiophene concentration during experiment HDS 2.

of the tests, the gasifier was running for more than five hours in order to guarantee stable conditions. The first test was done without HDS (reference test) in order to determine a reference value for catalyst deactivation. This test lasted for 260 h. At the first overall system test (HDS 1), the ZnO-adsorbent was not working properly due to previously occurred deactivation of the sorbent. Therefore the H₂S-value reached at the inlet of the Ni-catalyst was 5.1 ppm_v. This value was significantly higher than the expected equilibrium concentration of less than 1 ppm. Before starting the second HDS-experiment (HDS 2) a new ZnO-adsorbent was filled into reactor 2. The H₂S-values downstream the adsorbent in reactor 2 were far below 1 ppm.

Table 1 shows the average dry and wet synthesis-gas composition at all four sampling points in experiment HDS 2. The measured synthesis-gas composition at the gasifier (SP 1), the HDS-catalyst (SP2) and the desulfurization-reactor (SP 3) show almost the same

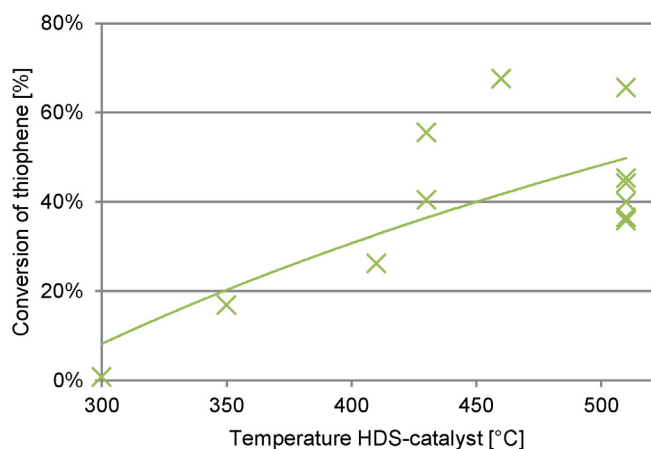


Fig. 7. Conversion of thiophene via HDS-catalyst.

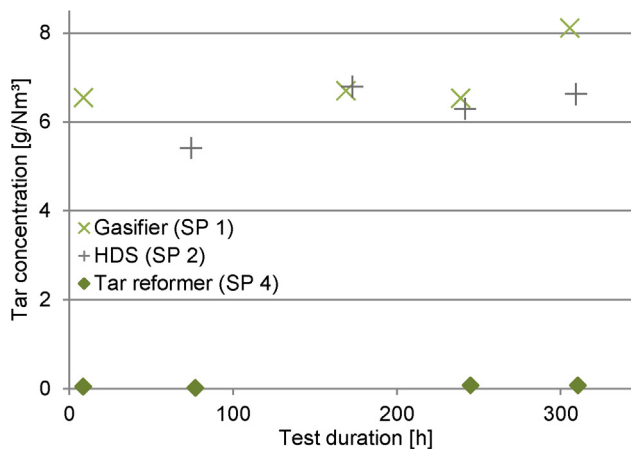


Fig. 9. Tar concentration during experiment HDS 2.

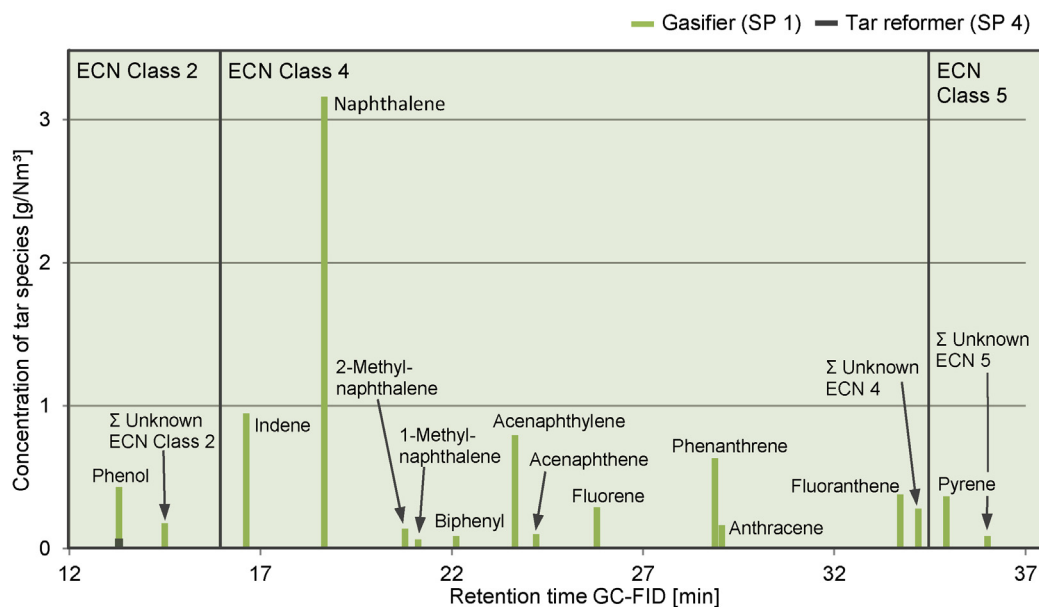


Fig. 10. Conversion of tars by catalytic tar reforming.

values except the H_2S -concentration. The average increase in H_2S due to the hydrogenation of organic sulfur species between SP 1 and SP 2 is 0.4 ppm_v. This is much lower than expected from the specific HDS-tests. In those tests, at 450 °C a H_2S -increase of around 1 ppm_v was measured. Comparing this to HDS 1, one can recognize that the H_2S increase was much higher in the HDS 1-test due to the reasons already discussed in Section 3.2. In HDS 1 a new catalyst was used. After running this experiment for 160 h the increase was still 2 ppm and stable. The reason for this behavior was not investigated in detail, but it indicates an activity loss of the HDS-catalyst.

In Table 1 (SP 3: desulfurization) it also is shown that the ZnO-adsorbent in reactor 2 worked properly at the HDS 2 test at a bed temperature of 300 °C. The H_2S -concentration measured at sampling point 3 downstream the desulfurization reactor was 0.1 ppm. This indicates that the adsorption equilibrium of H_2S on ZnO at 300 °C was reached.

The permanent gas composition downstream the tar reformer (SP 4) represents the equilibrium composition at approximately 500 °C of methanation-reaction (Eq. (1)), water-gas shift-reaction (Eq. (3)) and Sabatier-reaction (Eq. (4)) occurring in the tar reformer. If reactor 3 is operated in cooled mode, a methane-rich synthesis-gas would be produced [8]. The H_2S -concentration downstream the Ni-catalyst is below the detection limit of the analytics.

Fig. 8 shows the concentration of thiophene at HDS 2 test. When measured at the same time, the concentrations were lower downstream the HDS-reactor compared to the values after the gasifier. This indicates that the HDS catalyst is active, but its activity is low in comparison to the specific HDS-tests at this temperature. The thiophene concentration rose with increasing test duration, while the permanent gas composition and the tar concentration (cf. Fig. 9) stayed constant during the experiment. As already explained, this

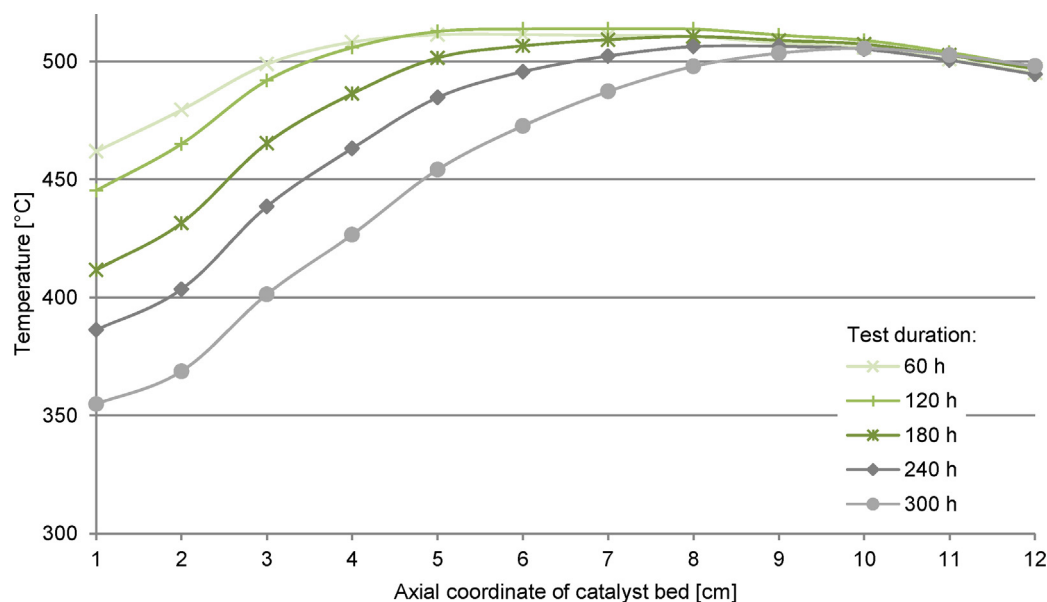


Fig. 11. Temperature profiles in tar reforming reactor (reactor 3).

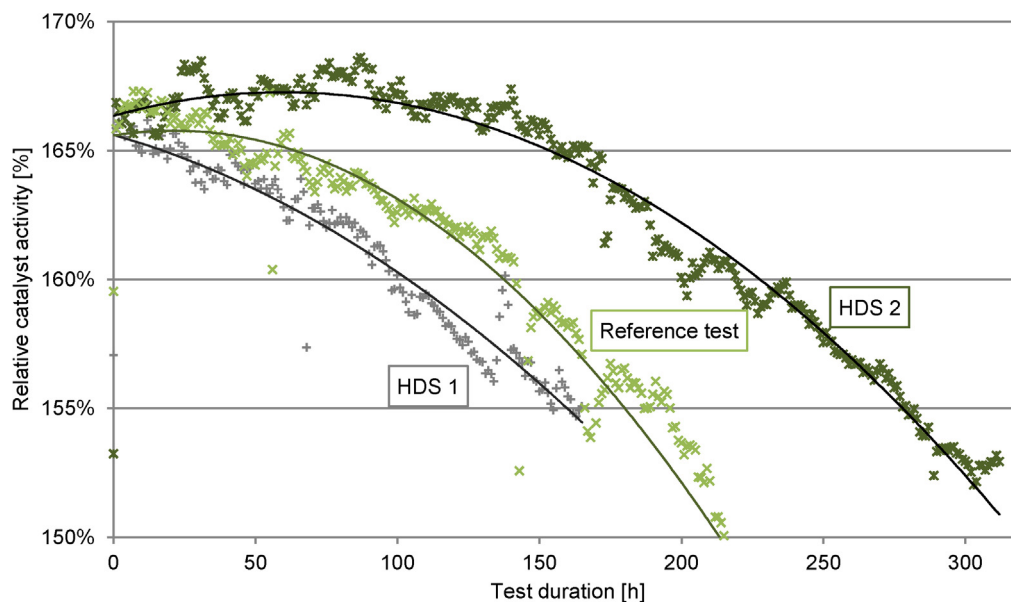


Fig. 12. Comparison of activity-decrease.

indicates an ongoing deactivation of the HDS-catalyst. However, work in ongoing in order to determine this deactivation behavior.

The tar concentration in the synthesis-gas is shown in Fig. 9, it includes GC-detectable tars, but benzene, toluene and xylene (BTX) are excluded. These volatile species do not affect the downstream facilities as they stay gaseous at their partial-pressure in the tested conditions. As it can be seen in the diagram, the tar loading at the sampling points 1 and 2 (gasifier and HDS) varied only insignificantly, the mean value was 6.5 g/m^3 in standard conditions. Downstream the tar reformer the tar concentration was below 0.1 g/Nm^3 , this leads to tar conversion rates higher than 98%.

The concentrations of the single tar components up- and downstream the tar reformer after 310 h on stream are shown in Fig. 10; they are sorted by their GC-FID retention-time, which means that species with a higher molar mass appear at later retention times. The main species in the synthesis-gas is naphthalene which can be converted completely at the Ni-catalyst. The species with the lowest conversion rates of around 80% are phenol and phenolic components.

Due to the exothermic methanation reaction (1) the almost adiabatic gas-cleaning reactor heats up to over 500°C . This increase in reactor temperature was measured as an axial temperature profile in reactor 3 according to Fig. 11. The continuously measured temperature-profile is used for determining the activity of the catalyst. Fig. 11 shows the variance of the temperature profile along the run-time of the HDS 2-test. The area under a particular temperature (t in $^\circ\text{C}$) profile in respect to the area of an inert temperature profile at 300°C (see Fig. 11) is a measure of the catalysts activity.

$$A = \frac{\sum_{n=1}^{11} (t_n + t_{n+1})/2}{11 \cdot t_{\text{inert}}} \quad (17)$$

The relative catalyst activities A (Eq. (17)) for the reference test and the two HDS-tests are compared in Fig. 12 as a function of test-duration. The reference test was carried out without HDS, with desulfurization by means of ZnO down to 0.1 ppm upstream the Ni-catalyst. At the HDS 1-test a HDS Co–Mo catalyst was used, but H_2S was not adsorbed on the ZnO as expected. The relative catalyst activity, due to the enhanced sulfur deactivation of the Ni-catalyst, decreased faster than at the reference test. In the third test (HDS 2), the desulfurization with ZnO was working correctly, the catalyst decreased slower compared to the reference test. This shows the

positive effect of the upstream HDS-catalyst in the tar reforming catalyst.

The catalyst deactivation rate Σ is calculated according to Eq. (18). For its calculation the decrease of catalytic activity and the test duration are used. Further the mass of the Ni-catalyst m_{catalyst} , the synthesis-gas volume flow \dot{V}_{gas} and the lower heating value LHV of the synthesis-gas, calculated from the permanent gas composition have to be known. The catalyst activity loss ΔA in Eq. (18) is calculated, as described in Eq. (19), from the catalyst activities at the beginning and the end of the observed period $\Delta\tau = \tau_2 - \tau_1$. In Eq. (19) A_1 and A_2 are the relative catalyst activities at the correspondent test duration τ_1 and τ_2 as shown in Fig. 12. A_{start} is the maximum activity at the beginning of the experiment. The value A_{inert} is 100%, this means no catalytic activity.

$$\Sigma \text{ (g/kWh)} = \frac{m_{\text{catalyst}} \text{ (g)}}{\dot{V}_{\text{gas}} \text{ (Nm}^3/\text{h}) \cdot \Delta\tau \text{ (h)} \cdot \text{LHV (kWh/Nm}^3\text{)}} \cdot \Delta A \quad (18)$$

$$\Delta A = \frac{A_2 - A_1}{A_{\text{start}} - A_{\text{inert}}} \quad (19)$$

Calculating the above mentioned catalyst deactivation gives the values shown in Fig. 13. The occurring H_2S -related deactivation at

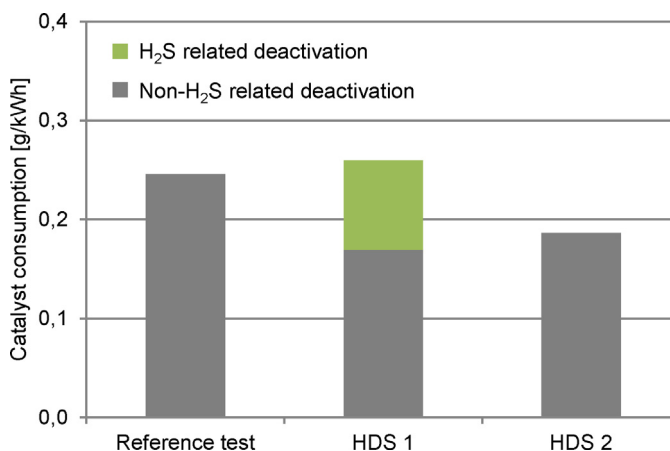


Fig. 13. Comparison of catalyst consumption.

the HDS 1-test can be separated from the non-H₂S-related deactivation by comparing this value to the HDS 2-experiment where the desulfurization with ZnO was working properly. Compared to the reference test, the use of an upstream HDS-catalyst decreases the non-H₂S related catalyst consumption in the tar reforming process significantly. Due to the limited conversion of thiophene, there is still a deactivation caused by sulfur poisoning at the Ni-catalyst. Deactivation caused by the formation of coke or carbon also occurs.

4. Conclusion and perspective

The aim of this work was the optimization of a medium temperature catalytic tar-reforming process using a Ni-catalyst with an upstream ZnO-desulfurization. Therefore a catalytic conversion of organic sulfur species to H₂S (HDS) was tested at realistic conditions. The tests were done with a synthesis-gas produced with a lab-scale, fluidized-bed gasifier operated with steam as fluidization- and gasifying-agent. The specific HDS-tests showed a limited conversion of thiophene to H₂S and no measurable activity of the Co–Mo catalyst for the hydrogenation of unsaturated hydrocarbons. The catalyst showed activity at temperatures above 350 °C. Activity increased with rising catalyst temperature, but a complete conversion of organic sulfur compounds was not possible. The maximum conversion rate was about 65% at 460 °C and 510 °C. Overall system tests showed that the use of a HDS-catalyst has a positive influence on the consumption of the Ni-catalyst used for tar reforming. The deactivation of the Ni-catalyst could be reduced by 20%.

The HDS-catalyst probably would work better if the GHSV is much lower, as the experiments of Rabou and Bos [21] showed. But the amount of catalyst needed would lead to higher investment costs. Further investigations with lower GHSV-values are necessary to evaluate the economic effects. It also may be useful if the H₂S in the synthesis-gas would be removed upstream the HDS-reactor due to reasons of a more suitable chemical equilibrium in the reactor. But due to the different operation temperatures of the ZnO-adsorbent at 300 °C and the HDS-catalyst at over 400 °C this means that the synthesis-gas must be cooled down first and be heated up again for HDS. The feasibility of this process management is not given because of increasing plant complexity and investment costs. The deactivation of the HDS-catalyst was not investigated in this work, but there was evidence of activity loss during the experiments. Further investigations are ongoing; also the test of the HDS-catalyst at a lower GHSV-value is planned. In future also the

adsorptive removal of organic sulfur by special sulfur adsorbents will be investigated.

Acknowledgement

The research discussed here was done in the course of the e!MISSION-project “InnoGasClean” (project number: 3343351) funded by the Austrian Research Promotion Agency FFG, the authors thank the agency for the kind financial support.

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